A New Approach to Modeling the Cure Kinetics of Epoxy Amine Thermosetting Resins. 2. Application to a Typical System Based on Bis[4-(diglycidylamino)phenyl]methane and Bis(4-aminophenyl) Sulfone

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ABSTRACT: Differential scanning calorimetry in dynamic and isothermal modes was used to study the cure kinetics of the commercial epoxy system Narmco 5208, whose main components are bis[4-(diglycidylamino)-phenyl]methane and bis(4-aminophenyl) sulfone. The data were analyzed in terms of a new mechanistic approach described in the preceding paper. The treatment explicitly takes into account both the epoxide–amine reactions and the subsequent etherification reaction. The kinetics can be completely described in terms of three rate constants, which obey the Arrhenius relationship. Excellent agreement with the experimental data is obtained if the etherification reaction is assumed to be first order with respect to the concentrations of epoxide groups, hydroxyl groups, and the tertiary amine groups formed in the epoxide–amine reaction. This model applies over the whole range of conversion up to the point where the resin vitrifies and the reaction becomes diffusion-controlled. The effect of the diffusion control is described very well by an approach based on simple equations proposed in the literature. Altogether, the model allows accurate prediction of the degree of conversion over the whole range of cure and over the temperature range 160–200 °C, which covers the usual curing conditions. Although the rate constants derived are specific to Narmco 5208, the model itself is generally applicable to other epoxy amine systems.

Introduction

Background. Mathematical modeling of the forming process in composite materials can lead to significant savings with respect to the amount of experimental work involved in determining the optimum processing conditions for a particular part.[1] For thermoset matrices such as epoxy resins, probably the most important aspect of the model is an accurate description of the polymerization reaction kinetics. Because of the complexity of the chemistry involved, existing models are usually semiempirical approximations, which work with varying degrees of success. The work to be described herein was undertaken with the aim of developing an accurate kinetic model for the commercial product Narmco Rigidite 5208. Because the existing models that were tried were found to work less well than desired, a new mechanistic approach was developed as described in the preceding paper.[2] In this paper, we describe its application to the Narmco 5208 system and demonstrate that it provides an excellent description of the curing kinetics.

Narmco 5208. Narmco Rigidite 5208, produced by BASF Narmco Division, is reported to consist of three components.[3] The main one is an epoxy resin based on tetraglycidyldiaminodiphenylmethane (TGDDM); a well-known commercial product of this type is Ciba-Geigy's Araldite MY 720. The second component is the primary amine curing agent diaminodiphenylsulfone (DDS), also available from Ciba-Geigy as Hardener HT 976. These two monomers also form the basis of several other commercial products. The third component of Narmco 5208 is an epoxy resin based on a bisphenol A Novolac; such a product is sold by Celanese under the name Epi-Rez SU-8.

Previous Work. The general nature of the epoxy amine reaction and some well-known equations used to describe the kinetics have been discussed in part 1 of this series.[2] Barton[4] has reviewed much of the literature. There have been numerous studies of mixtures of TGDDM and DDS and of commercial systems containing these products.[5–21] These have involved different approaches to describing the kinetics, with varying degrees of success. In some cases, a good fit to experimental data was obtained in the early stages of the reaction, but deviations were observed in the later stages. In other cases, reasonably good overall agreement was obtained but only by taking a phenomenological approach in which empirical parameters are introduced and varied to fit the data. It appears to be well established that the etherification reaction is significant and cannot be ignored.[4] One question that has not been satisfactorily resolved, however, is that of the relative reactivities of the primary amine groups initially present and the secondary amine groups formed in the reaction. While it is frequently stated that the secondary amine groups are much slower to react, the evidence for this is not entirely convincing. Gupta and co-workers[8] used differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), and electron spin resonance (ESR) to study mixtures involving TGDDM, DDS, and the secondary amine DMDDS (bis[4-(methylamino)phenyl] sulfone). They concluded that in the early stages of cure the main reaction is between primary amine and epoxide (PA–E), that the reaction between secondary amine and epoxide (SA–E) is negligible, and that the cure is completed by the hydroxyl–epoxide (OH–E) reaction. The rate constant for the latter was estimated to be an order of magnitude smaller than the PA–E rate constant, and the enthalpy of reaction about eight times less. However, Barton[17] has provided conflicting data showing that TGDDM–DDS mixtures with amine/epoxide ratios ranging from 0.61 to 1.14 have a constant enthalpy of reaction of about 110 kJ/mol of epoxide. This suggests that both primary and secondary amine groups react completely with epoxide and that residual epoxide is consumed by the OH–E reaction, all these reactions having approximately equal exothermicity. The calorimetric data of

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Gupta et al. may also be interpreted in this way. Furthermore, their results concerning the ratio of the sulfone peaks at 1150 and 1105 cm^{-1} in the IR spectrum may also be subject to other interpretations. Morgan and others[9-11] have also studied the mechanism of TGDDM-DDS curing by means of FT-IR spectroscopy. Their data indicated that the epoxide homopolymerization reaction is some 200 times slower than the PA-E reaction. The SA-E reaction was assumed to be about ten times slower, on the basis of data obtained by Bell[22] for the reaction of DGEBA (diglycidyl ether of bisphenol A) with MDA (methylenedianiline). Similarly, the OH-E reaction was also assumed to be ten times slower, on the basis of the above-mentioned work of Gupta et al.[7,8] While these assumptions appear to be in agreement with their results, this does not constitute proof that they are valid, since the data may not be sufficiently sensitive. In fact, some of their data[11] suggest that the SA-E reaction is rather significant, and the recent work by Zukas et al.[12] indicates that the primary and secondary amine groups have approximately equal reactivity. This important question will only be resolved by further experimental work, preferably involving a technique that can directly quantify the different types of amine groups.

Published data for Narmco 5208 are rather limited. Cizmecioglu and Gupta[6] studied the kinetics by dynamic DSC and analyzed the results in terms of a single *n*th-order reaction. This is an oversimplification, since it has been clearly established that the epoxy-amine reaction is autocatalytic and that etherification can also be important.

Recently, Chiao[21] has analyzed the TGDDM-DDS data of Mijovic et al.[15] in terms of a mechanistic model incorporating an epoxide-hydroxyl reaction in addition to the epoxide-amine reactions. The kinetic equations were not solved analytically, so a numerical solution was used to fit the data, and good agreement was obtained. No assumption was made concerning the relative reactivity of the secondary and primary amine groups. However, in order to limit the number of parameters to be fitted to a reasonable number, the ratios of the rate constants for catalysis by hydroxyl groups formed in the reaction and for catalysis by impurities initially present were fixed at values obtained by analyzing earlier data[23] for the reaction between phenyl glycidyl ether and diethylamine or *n*-butylamine. The apparent activation energies obtained for the PA-E, SA-E, and OH-E reactions were respectively 55.1, 71.6, and 97.2 kJ/mol.

Experimental Section

Materials. In addition to the composite Narmco 5208, some mixtures of the individual components known to be present in this system were studied. Samples of Araldite MY 720 and Hardener HT 976 were obtained from Ciba-Geigy and Epi-Rez SU-8 from Celanese. The epoxide content of the resins was determined by reacting the resin with excess hydrochloric acid in acetone/water solution and then titrating the excess acid with sodium hydroxide. The equivalent weights obtained were 130.2 (σ = 2.1%) for MY 720 and 227.3 (σ = 0.4%) for SU-8. These are in good agreement with the typical values reported by the manufacturers for these materials (117-134 for MY 720, 215 for SU-8). For the Hardener HT 976, which is near 100% pure, the equivalent weight was calculated to be 62.1. This is based on the assumption that each of the four N-H bonds present can react with an epoxide group.

The prepreg studied was Narmco Rigidite 5208/WC3000-42 from Narmco Materials Inc. It consists of woven carbon-fiber reinforcement impregnated with Narmco 5208 resin to a nominal resin content of 42% by weight. The recommended cure schedule involves a 1-h dwell at 135 °C followed by a 2-h cure at 177 °C. The volatiles content, measured by weighing samples before and after heating at 177 °C for 20 min, was found to be 1.90 ± 0.03%, based on total prepreg weight.

The prepreg as received is partly polymerized, or "B-staged". As pointed out by Roberts,[1] for accurate modeling of the cure it is essential to characterize the initial chemical state of the resin, i.e., its composition and initial degree of advancement (polymerization). This was done by reverse-phase liquid chromatography.[24] Different mixtures of MY 720, SU-8, and HT 976 were prepared in acetone solution and the acetone was removed under vacuum without heating. Samples were then polymerized to two different degrees of advancement by heating at 120 °C for 30 and 80 min. Analysis by RPLC gave chromatograms in which the areas of the following four peaks could be measured: TGDDM (main component of MY 720), DDS (HT 976), DGEBA = diglycidyl ether of bisphenol A (major component of SU-8), and the initial reaction product between TGDDM and DDS. These quantities were then related to the mixture composition and degree of advancement. On analyzing the Narmco 5208 resin and comparing its chromatogram to that of the calibration mixtures, its composition was estimated to be 65.9% by weight MY 720, 13.2% SU-8, and 20.9% HT 976, and the initial degree of polymerization α_0 in the prepreg as received was 0.038. This composition corresponds to an initial amine-to-epoxide ratio B equal to 0.60, based on the epoxide equivalent weights reported above.

Some binary and ternary mixtures of MY 720, SU-8, and HT 976 were also studied by DSC. These were prepared by dissolving precisely weighed quantities of the materials in acetone, pouring the solution into a shallow aluminum dish, and evaporating the acetone under vacuum without heating.

Thermal Analysis. The prepreg cure was studied by both dynamic and isothermal DSC[4] on a Setaram Model CDP111 calorimeter. Dynamic runs were done on both prepared mixtures and prepreg. Approximately 50 mg of sample was placed in an open platinum crucible that was suspended vertically in the calorimeter. An empty crucible was used as the reference. The sample was heated in a nitrogen atmosphere at a fixed rate of 5 °C/min from room temperature to around 300 °C, at which point some decomposition is observed. In the case of prepreg samples, the exact weight of resin present after the DSC run was determined by thermogravimetric analysis (TGA) on a Setaram B70 thermobalance equipped with a graphite resistance furnace. The sample was heated in an oxygen atmosphere at 10 °C/min from room temperature to 900 °C.[25]

Isothermal DSC runs were done on prepreg only, at temperatures ranging from 160 to 210 °C. For these experiments the sample size was around 100 mg and unsealed aluminum crucibles were used. In order to minimize the time required for equilibration after the sample is introduced into the calorimeter, a warming oven was added to preheat both sample and reference for about 10 min at 125 °C before introduction into the main oven. RPLC analysis indicated that less than 0.5% of the epoxide groups react during this treatment. The reference consisted of a crucible containing fully polymerized prepreg, and sample and reference weights as well as the corresponding crucible weights were matched as closely as possible. The calorimeter signal (heat flux = dQ/dt) was measured for about 6-7 h, except at 210 °C where 1.5-2 h was sufficient. After each isothermal run, a dynamic run was performed on the same sample to complete the polymerization and determine the residual heat of curing. Three runs were done at each temperature.

The digitized data were acquired by a Hewlett-Packard HP-85 computer and subsequently transferred to a VAX 11/750 or an Apple Macintosh for further treatment.

In isothermal DSC, there is a brief period of temperature equilibration after the sample is introduced into the instrument. In order to estimate the time required by the calorimeter to give a meaningful signal, a few samples were run twice, the first run giving the raw polymerization curve, the second giving the corresponding experimental baseline, which is then used to correct the raw curve.[4] It was found that the shapes of the raw and corrected curves are identical after about 2 min and are only slightly different before the point where the signal becomes exothermic. Since the time required to obtain the experimental baseline can be quite high (up to 6-7 h), the extrapolation method used by Barton[17] was also tried. In this case, the baseline was

Table I
Dynamic DSC Data for the Mixtures Involving MY 720, HT 976, and SU-8

mixture	MY 720, %	HT 976, %	SU-8, %	amine-to-epoxide ratio	T_{max}, °C	ΔH,[a] J/g	ΔH, kJ/mol of epoxide
1	77.97	22.03	0	0.59	252	643.7 (5.4)	107.5
2	77.02	22.98	0	0.63	250	637.9 (3.9)	107.8
3	73.17	26.83	0	0.77	234	605.2 (5.9)	107.7
4	68.99	31.01	0	0.94	220	563.3 (3.7)	106.3
5	67.58	32.42	0	1.01	218	556.3 (4.5)	107.2
6	77.78	13.17	9.05	0.33	267	657.5 (4.8)	103.2
7	68.92	22.05	9.03	0.62	250	595.7 (4.1)	104.7
8	59.49	31.54	8.97	1.02	217	533.3 (4.6)	107.4
9	68.80	13.13	18.08	0.35	268	623.5 (3.0)	102.6
10	59.73	22.27	18.00	0.67	248	565.6 (7.8)	105.2

[a] Values in parentheses correspond to standard deviations based on three determinations.

obtained by horizontal extrapolation using the last ten points of the curve, and the point where it intersects with the onset of the reaction exotherm was taken to be the starting time of the reaction ($t = 0$). The total heats of polymerization obtained by the two methods of baseline correction were identical within less than 1%. Consequently, the extrapolation method was chosen for correction of all the experimental curves. These experiments showed that the points obtained within the first 2 min of the polymerization run are subject to some error, and their ordinate values (dQ/dt) are lower than the real values.

Results and Discussion

Mixtures. Dynamic DSC. In order to relate the epoxide conversion to the heat evolution in the DSC experiment, it is necessary to assume that the heat released on reaction of an epoxide group is the same regardless of the type of epoxy or the nature of the reaction. To confirm this hypothesis, several mixtures of MY 720, HT 976, and SU-8 were analyzed by dynamic DSC. The results are given in Table I. The mixtures cover a range of compositions and amine-to-epoxide ratios. Attempts to analyze some binary mixtures of SU-8 and HT 976 were unsuccessful. First, it is difficult to remove all the acetone without heating the mixture. Second, it is believed that the higher functionality of SU-8 leads to rapid vitrification, which causes the reaction to stop well before completion.

Figure 1 shows the DSC curves for three different mixtures of MY 720 and HT 976 with varying amine-to-epoxide ratios. The effect on the nature of the reaction is evident. Mixture 5 (Figure 1a) is a stoichiometric mixture in which the number of epoxide rings is just sufficient to react with all the N–H bonds present: hence the amine-epoxide reaction is believed to be the dominant one. The DSC curve shows a strong exothermic peak with a maximum at 218 °C. In mixture 3 (Figure 1b), there is a 30% excess of epoxide groups with respect to amine, and these are believed to polymerize by etherification. This occurs at a somewhat higher temperature and substantially broadens the DSC exotherm peak; the maximum now occurs at 234 °C. In mixture 2 (Figure 1c), there is a 60% excess of epoxide groups. The etherification reaction becomes even more important and shifts the peak maximum to 250 °C.

The other mixtures gave similar curves, and the results are summarized in Table I. The temperature at which the peak maximum occurs is highly dependent on the overall amine-to-epoxide ratio but is not significantly affected by the replacement of part of the MY 720 by SU-8. A plot of T_{max} versus the amine–epoxide ratio gives a good linear relationship (squared correlation coefficient 0.982). The enthalpies of polymerization for the different mixtures were determined by computer integration of the exotherm peak using a linear baseline. The results, based on three to four determinations for each mixture, are listed in the table. The values vary with the mixture, but if they are converted to kilojoules per equivalent of epoxide present, a constant value of about 107 kJ/mol is obtained. This is in excellent agreement with the results reported by Barton.[17] The fact that the same result is obtained for mixture 5, where most of the epoxide groups react with amine, and mixture 2, where at least one-third react by etherification, indicates that the enthalpies for these two reactions are very similar. Likewise, comparison of mixtures 1 and 10 suggests that the enthalpy for the SU-8 is not much different from that for the MY 720. Both mixtures have similar amine-to-epoxide ratios, but mixture 1 contains no SU-8, while in mixture 10, 14% of the epoxy groups come from SU-8. The two mixtures with very low amine-to-epoxide ratios (0.33 and 0.35) give slightly lower enthalpies of reaction. This could be due to incomplete reaction because of the large excess of epoxide groups.

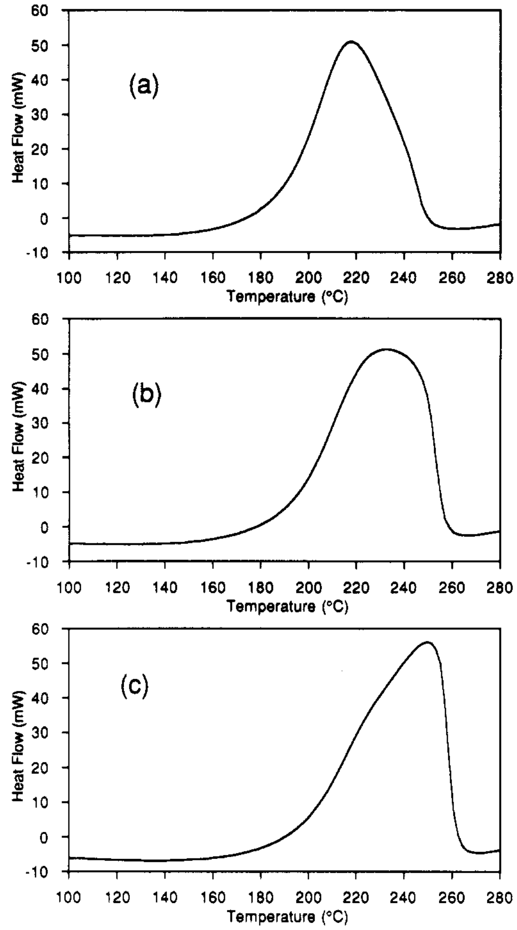

Figure 1. Dynamic DSC curves for mixtures of MY 720 and HT 976 with amine-to-epoxide ratios of (a) 1.01, (b) 0.77, and (c) 0.63; heating rate 5 °C/min.

Prepreg. Dynamic DSC. Five specimens of Narmco 5208 prepreg were analyzed by dynamic DSC and TGA as described in the Experimental Section. The DSC curve is very similar to Figure 1c, with a maximum around 250 °C. The average weight loss during the DSC experiment was 2.1 ± 0.5%, which is close to the value of 1.9% determined for the volatiles content. This indicates that the amount of degradation that occurs is negligible and that the weight loss is mainly due to nonreactive volatiles such as water and acetone, which are known to be present in the prepreg. For each specimen, the weight of resin remaining after the DSC experiment was determined by TGA and this was taken to be the true weight of resin in the prepreg, exclusive of volatiles. The energy released on polymerization was determined by integrating the DSC peak and was then divided by this weight to give the enthalpy of polymerization ΔH. The average of the five values was 620.4 J/g, with a standard deviation of 7.5 J/g. It was pointed out in the Experimental Section that this resin is partly polymerized, or B-staged, to the extent of 0.038; in other words, 3.8% of the epoxide groups initially present in the system have already reacted. Thus, for completely unreacted Narmco 5208, ΔH would be 620.4/(1 − 0.038) or 645.1 J/g. On the basis of the other results given in the Experimental Section, the enthalpy per epoxide group is calculated to be 114.3 kJ/mol. This is slightly higher than the value of 107–108 kJ/mol reported in Table I for prepared mixtures but within the range 100–118 kJ/mol typically observed for epoxide ring opening.[26] The average fiber content of the prepreg for the five specimens analyzed was 59.0 ± 0.9% by weight.

Prepreg. Isothermal DSC. Three experiments were performed at each of six temperatures ranging from 160 to 210 °C in 10-deg increments. A typical curve, showing heat flow ($\mathrm{d}Q/\mathrm{d}t$) as a function of time at 160 °C is given in Figure 2a. This curve has been corrected by means of the extrapolation method described in the Experimental Section. Integration gives the evolved heat as a function of time:

$$Q(t) = \int_0^t \mathrm{d}Q/\mathrm{d}t\,\mathrm{d}t \qquad (1)$$

The total heat evolved during the isothermal experiment is given by the total area under the isothermal curve:

$$Q_\mathrm{i} = \int_0^{t_\mathrm{f}} \mathrm{d}Q/\mathrm{d}t\,\mathrm{d}t \qquad (2)$$

where t_f is the time corresponding to the end of the experiment, when the rate of heat evolution becomes negligible. Since the polymerization may not be complete after the isothermal run, it is completed in the subsequent dynamic run, as shown in Figure 2b. Integration of this curve gives the residual heat of polymerization Q_r. At higher temperatures, the isothermal cure occurs much faster, a higher degree of polymerization is achieved, and Q_r is lower.

In order to analyze the kinetics, the curves must be expressed in terms of α, the degree of polymerization. To do this, the usual assumption was made, namely, that the heat evolved is directly proportional to the number of epoxide groups reacted, regardless of the type of reaction. As discussed above, the results for the various prepared mixtures support this assumption.

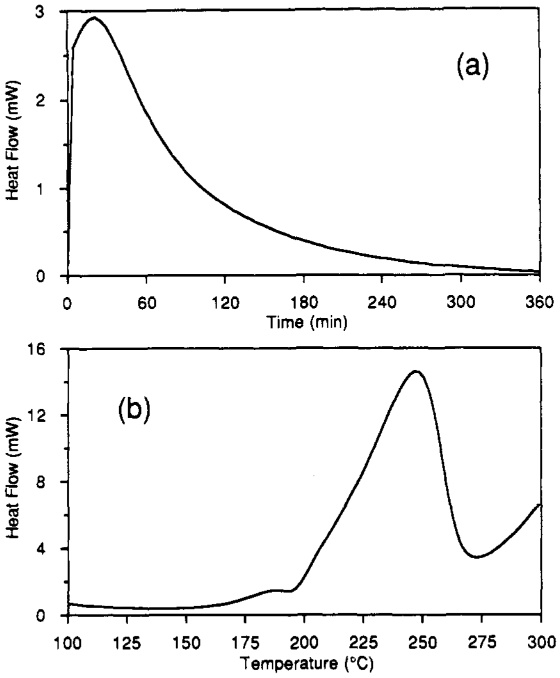

Figure 2. DSC curves for Narmco 5208 prepreg: (a) isothermal run at 160 °C; (b) dynamic curve recorded after isothermal run, heating rate 5 °C/min.

In most analyses of the kinetics of prepreg systems, it is assumed that the extent of B-staging is negligible, that is, that the degree of polymerization at the beginning of the cure (α_0) is equal to zero. In this work, the initial degree of cure, determined by liquid chromatography to be equal to 0.038, was taken into account in the analysis. This leads to the following equations for deriving α and $\mathrm{d}\alpha/\mathrm{d}t$ as functions of time:

$$\alpha(t) = \alpha_0 + \left(\frac{1-\alpha_0}{Q_\mathrm{i}+Q_\mathrm{r}}\right)Q(t) \qquad (3)$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{1-\alpha_0}{Q_\mathrm{i}+Q_\mathrm{r}}\right)\frac{\mathrm{d}Q}{\mathrm{d}t} \qquad (4)$$

With these data it is possible to construct a curve of $\mathrm{d}\alpha/\mathrm{d}t$ versus α for each temperature. These are then used to test the kinetic model. Of the several thousand points in a given curve, 50–100 were selected at equal intervals for this analysis.

Analysis of the Data by Means of Some Existing Models. The first test applied to the data involved the simplified Horie equation:[27]

$$\mathrm{d}\alpha/\mathrm{d}t = (K_1 + K_2\alpha)(1-\alpha)(B-\alpha) \qquad (5)$$

where the rate constants K_1 and K_2 correspond respectively to catalysis by groups initially present in the resin and catalysis by hydroxyl groups formed in the reaction and B is the ratio of primary amine N–H bonds to epoxide groups in the initial mixture. Figure 3 shows plots of the reduced rate function $F_1(\alpha) = (1-\alpha)^{-1}(B-\alpha)^{-1}(\mathrm{d}\alpha/\mathrm{d}t)$ versus α for three different temperatures. This should give a straight line with intercept K_1 and slope K_2. The value of B was fixed at 0.6, as determined by liquid chromatography. Except for the first few points, linear behavior is observed up to α about 0.2, with slight deviation between 0.2 and 0.3 and significant deviation beyond this point. The deviation observed at higher temperatures for the first few points can be explained by the fact that these occur within the first 2 min of the experiment, before the system has fully equilibrated. The deviation observed when $\alpha > 0.3$ is attributed to the lack of validity of the model in this region, where the etherification reaction is believed to become significant. Linear regression was performed by using the points shown by filled symbols in the figure. The intercepts of these lines were used to determine the values of $\mathrm{d}\alpha/\mathrm{d}t$ corresponding to $\alpha = 0$.

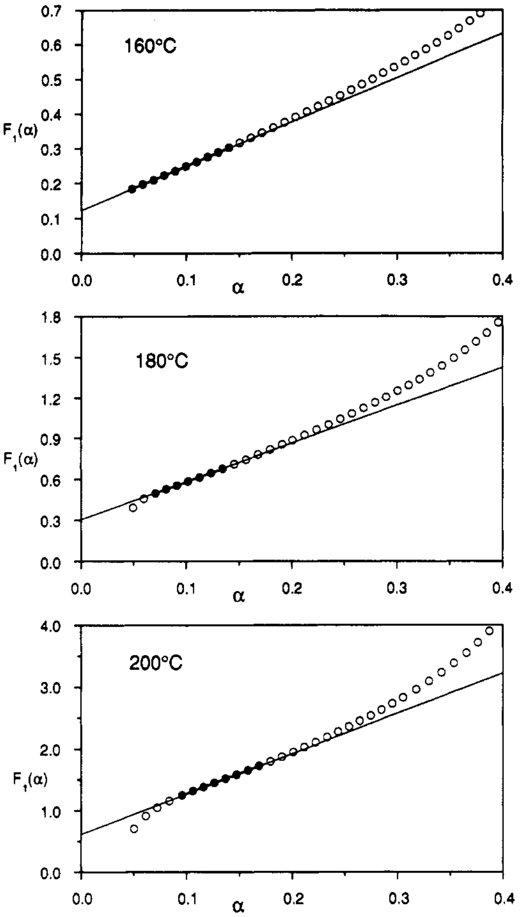

Figure 3. Plots of $F_1(\alpha) = (1-\alpha)^{-1}(B-\alpha)^{-1}(\mathrm{d}\alpha/\mathrm{d}t)$ as a function of α for three different temperatures; units s^{-1} x 1000.

An extension of this approach, used by Springer et al. for the commercial product Hercules 3501-6,[5] separates the reaction into two distinct stages. It is assumed that in the beginning ($\alpha < 0.3$) only the epoxide–amine reaction need be considered, and eq 5 is used. When the epoxide–amine reaction is complete, the epoxide–hydroxyl reaction takes over, and, since the hydroxyl concentration is now constant, the reaction is assumed to be first order with respect to epoxide concentration. Thus it can be described by the following equation:

$$\mathrm{d}\alpha/\mathrm{d}t = K_3(1-\alpha) \tag{6}$$

In this case the reduced function $F_2(\alpha) = (1-\alpha)^{-1}(\mathrm{d}\alpha/\mathrm{d}t)$ should be constant and equal to K_3. To test this hypothesis, the quantity $F_2(\alpha)$ was plotted against α as shown in Figure 4. Interesting behavior is observed. Only at the higher temperature of 200 °C could the approximation be considered to be valid, and, even then, only up to a certain point. Generally speaking, the quantity $F_2(\alpha)$ rises to a maximum value at around $\alpha = 0.3$, but instead of remaining constant it gradually declines until α reaches about 0.7 or 0.8. At this point there is a rather abrupt drop and the reaction rate falls to zero before completion. This is believed to be due to vitrification of the system and the onset of diffusion control. This will be discussed in more detail later. It is interesting to note that in Springer's work, although this approach gave a reasonably good fit to the experimental data for α up to about 0.6, in order to achieve it it was necessary to assume negative values for the rate constant K_2! The problem lies in the fact that Hercules 3501-6 is a complex mixture containing not only TGDDM and DDS but also two other epoxies as well as a boron trifluoride catalyst. As a result, the curve of $\mathrm{d}\alpha/\mathrm{d}t$ versus α does not clearly show the maximum typical of an autocatalytic reaction, which eq 5 was designed to represent.

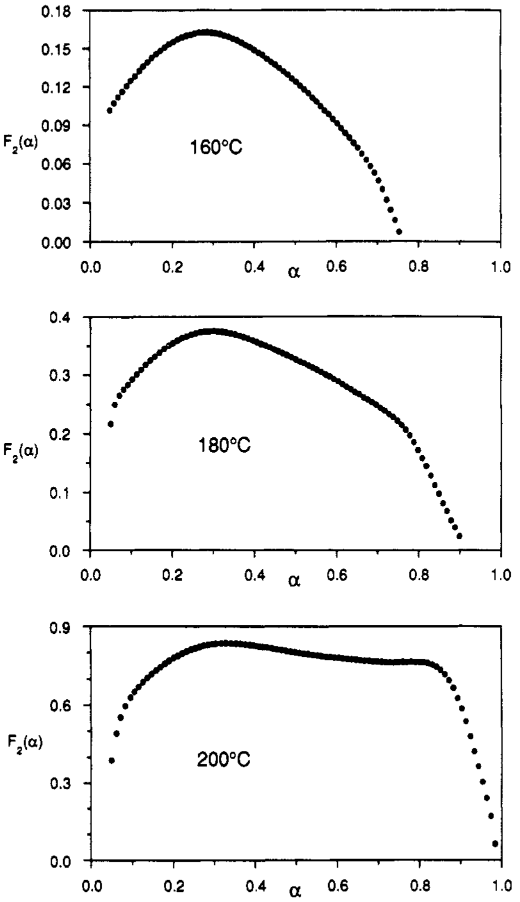

Figure 4. Plots of $F_2(\alpha) = (1-\alpha)^{-1}(\mathrm{d}\alpha/\mathrm{d}t)$ as a function of α for three different temperatures; units $\mathrm{s}^{-1} \times 1000$.

An attempt was also made to fit the data with the semiempirical equation proposed by Kamal:[28]

$$\mathrm{d}\alpha/\mathrm{d}t = (K_1 + K_2\alpha^m)(1-\alpha)^n \tag{7}$$

The four unknowns were determined so that the calculated and experimental data matched with respect to the following four values: (1) the initial value of $\mathrm{d}\alpha/\mathrm{d}t$, as determined from the intercepts in Figure 3; (2) $\alpha_{\max}$, the location of the maximum value of $\mathrm{d}\alpha/\mathrm{d}t$; (3) $(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$, the maximum value; (4) the value of $\mathrm{d}\alpha/\mathrm{d}t$ at $\alpha = 0.5$. The results are shown in Figure 5. At 160 °C, an excellent fit was obtained up to the point of vitrification. At 180 and 200 °C, the fit was good up to $\alpha = 0.5$ but poor beyond that point. Furthermore, the values of m and n varied significantly with temperature, as indicated in the figure. Equation 7 is thus less than ideal for this system.

Analysis of the Data by Means of the New Approach. The model developed in the preceding paper involves a more rigourous approach than those that have just been applied. It is a mechanistic approach in which the Horie model is extended to include the etherification reaction. The conversion of epoxide groups into ether groups is described by the following kinetic expression:

$$-\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{\mathrm{d[ether]}}{\mathrm{d}t} = k_3EH^mA_3{}^n \tag{8}$$

where E, [ether], H, and A_3 are the concentrations of epoxide, ether, hydroxyl, and tertiary amine groups, respectively. The exponents m and n (which should not be confused with those used in eq 7) allow for different

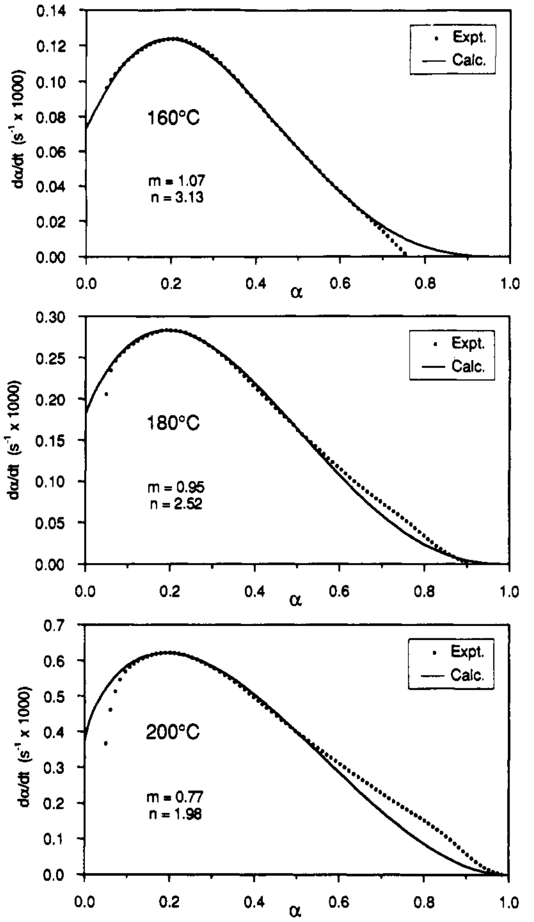

Figure 5. Results obtained on fitting experimental data for $d\alpha/dt$ versus α with eq 7.

Table II
Different Possibilities for the Etherification Reaction Mechanism

case	k_3 term	m	n	Z	nature of reaction
1	EH	1	0		epoxide–hydroxyl, uncatalyzed
2	EH^2	2	0		epoxide–hydroxyl, catalyzed by hydroxyl
3	EHA_3	1	1	1.5	epoxide–hydroxyl, catalyzed by all tertiary amine groups
4	EHA_3	1	1	0	epoxide–hydroxyl, catalyzed only by tertiary amine groups formed in reaction
5	E	0	0		homopolymerization, first order in epoxide
6	EA_3	0	1	1.5	homopolymerization, catalyzed by all tertiary amine groups
7	EA_3	0	1	0	homopolymerization, catalyzed only by tertiary amine groups formed in reaction

scenarios for the reaction mechanism as shown in Table II. The first corresponds to the case of an epoxide–hydroxyl reaction that occurs either without catalysis or with catalysis by groups whose concentration is constant and therefore may be incorporated into the rate constant k_3. The second is similar except that a second hydroxyl group accelerates the reaction, giving rise to an EH^2 term rather than EH. The third and fourth scenarios correspond to an epoxide–hydroxyl reaction catalyzed by tertiary amine groups. In this case, a distinction is made between the tertiary amine groups initially present in the system (in this case, in the TGDDM resin) and those produced by the epoxide–amine reaction. The coefficient Z is defined[2] as $2A_{30}/BE_0$, where A_{30} and E_0 are the initial concentrations of tertiary amine and epoxide. On the basis of two TA groups for every four TGDDM epoxide groups (but none for SU-8) and $B = 0.60$, Z is estimated to be 1.5 for Narmco 5208. Case 3 (with $Z = 1.5$) includes these in the calculation. Case 4 (with Z set to 0) assumes that only the tertiary amine groups produced in the epoxide–amine reaction catalyze the epoxide–hydroxyl reaction. Cases 5–7 correspond to etherification without the participation of hydroxyl groups, i.e., homopolymerization. This is assumed to occur either by a simple first-order reaction with respect to epoxide (case 5) or with the participation of tetiary amine groups as just discussed (cases 6 and 7).

The kinetics are described in terms of the following two variables:

$$\alpha = 1 - \frac{E}{E_0} \tag{9}$$

$$\beta = 1 - \frac{2A_1 + A_2}{2A_{10}} = \frac{H - H_0}{2A_{10}} \tag{10}$$

where A_1 is the concentration of primary amine groups, A_2 is the concentration of secondary amine groups, and the subscript "0" designates the initial value of the concentration to which it is attached. The variable α is the usual overall extent of conversion of epoxide groups. The variable β is equal to the fraction of primary amine N–H bonds that have reacted with epoxide groups to produce linkages containing hydroxyl groups; thus it is a measure of the extent of the epoxide–amine reaction. Together these two variables cover the two reaction pathways.

The kinetic equations can be solved[2] to give the following two equations:

$$\alpha = B\beta + \frac{K_3}{K_1 + BK_2}[C_1\beta + C_2\beta^2 + C_3 \ln(1 + R^{-1}\beta) + C_4 \ln(1 - \beta)] \tag{11}$$

$$d\alpha/dt = [B(K_1 + BK_2\beta)(1 - \beta) + K_3(Y + \beta)^m(Z + \beta^2)^n](1 - \alpha) \tag{12}$$

where K_1 is the rate constant for the epoxide–amine reaction catalyzed by groups initially present (including hydroxyl), K_2 is the rate constant for the same reaction catalyzed by hydroxyl groups formed in the reaction, K_3 is the rate constant for the etherification reaction, $Y = H_0/BE_0$, and $R = K_1/BK_2$. The coefficients C_1 to C_4 depend on the particular values of m and n and are given in Table II of the preceding paper. With these equations, although $d\alpha/dt$ cannot be expressed analytically in terms of α, the relationship between the two can be expressed in terms of a set of calculated points.

Regardless of the particular scenario, there are three rate constants that must be determined to best fit the experimental data for $d\alpha/dt$ as a function of α. Because the dependent variable $d\alpha/dt$ cannot be expressed as a simple function of the independent variable α, it is not possible to use standard regression techniques to determine the constants. Instead, an iterative procedure was used. After initial estimates for K_1, K_2, and K_3 were chosen, for each experimental value of α the corresponding value of β was calculated by numerical solution of eq 11. The values of α and β were then used in eq 12 to calculate $d\alpha/dt$. The coefficient Y (related to the initial hydroxyl content) was assumed to be negligible. The calculated values of $d\alpha/dt$ were compared with the experimental values and the rate constants were adjusted until the calculated and experimental curves matched according to the following three criteria: (1) They should have the same value of $d\alpha/dt$ when $\alpha = 0$; for this purpose, the experimental values

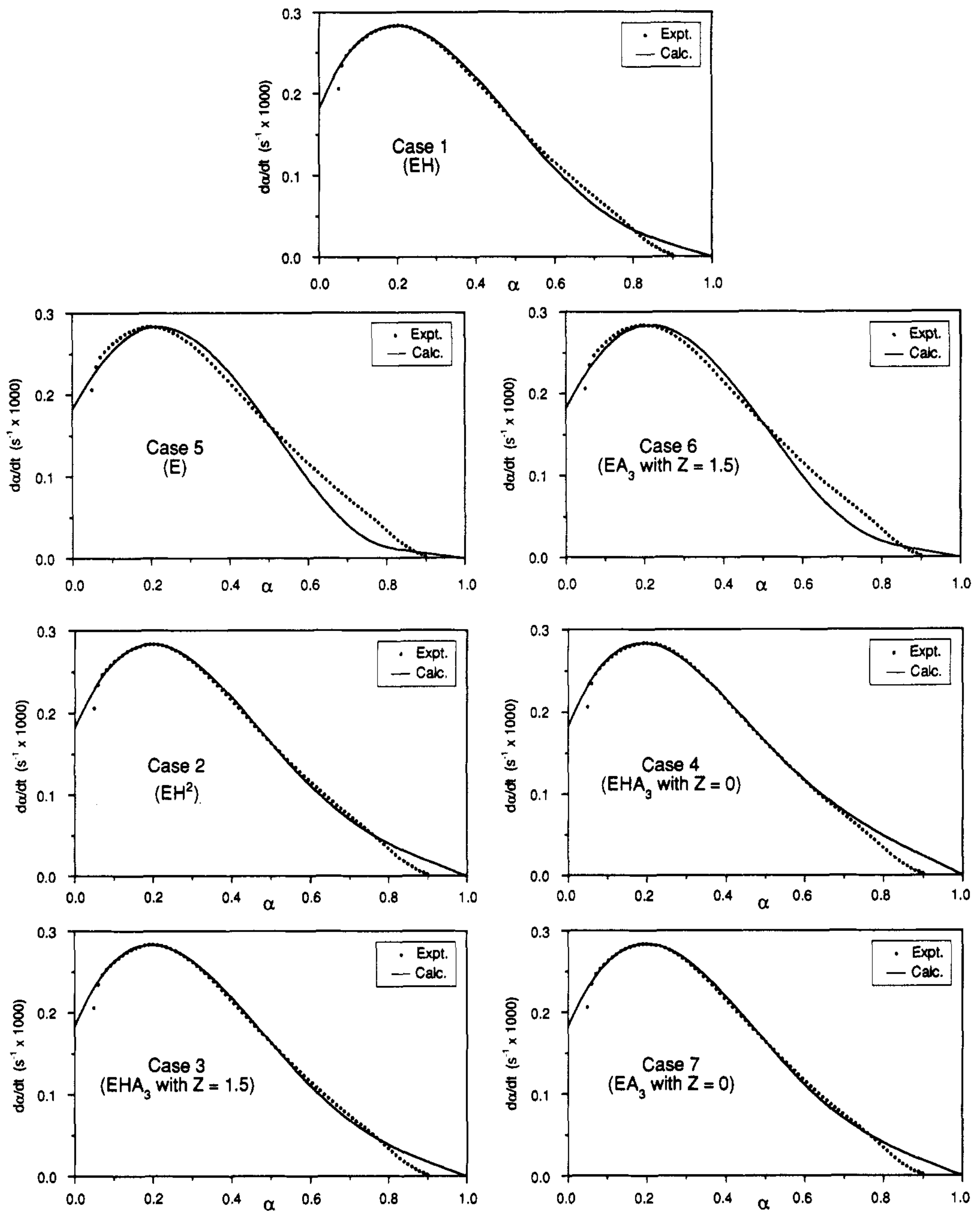

Figure 6. (a, Top) Comparison of experimental values of dα/dt with curves calculated according to cases 1, 5, and 6 of Table II, for one experiment at 180 °C. (b, Bottom) Comparison of experimental values of dα/dt with curves calculated according to cases 2–4 and 7 of Table II, for one experiment at 180 °C.

were obtained by extrapolation, based on the intercepts of the lines given in Figure 3. (2) The maximum calculated value of dα/dt should be the same as the maximum experimental value (but not necessarily at the same value of α). (3) The two curves should have the same values of dα/dt at $\alpha = 0.5$. Once the three rate constants that meet these criteria were found, the overall quality of the fit was judged by graphically comparing the calculated and experimental sets of data.

Figure 6 shows the results for the seven different scenarios applied to one set of data obtained at 180 °C. Three of the cases, shown in Figure 6a, gave rather poor fits. These include a bimolecular epoxide–hydroxyl reaction (case 1), uncatalyzed homopolymerization (case 5), and homopolymerization catalyzed by all tertiary amine groups (case 6). Of the remaining cases, depicted in Figure 6b, three gave a good fit but one was virtually perfect. (As already mentioned, the deviation observed for the first point or two is due to incomplete equilibration of the calorimeter, and the deviation observed at high values of α is due to vitrification of the resin.) The perfect fit corresponds to case 4, where the reaction is first-order with respect to epoxide groups, hydroxyl groups, and the tertiary amine groups formed in the reaction (but not those present in the TGDDM). Whether the slight difference between this case and the other three in Figure 6b is significant (i.e., whether case 4 corresponds to the true mechanism) needs to be confirmed by further experimentation. A possible explanation is given in the next section. Because the case 4 mechanism gives the best agreement, it was used to analyze the data and determine the three rate constants for all 18 experiments (three at each of the six temperatures studied).

As mentioned above, the deviation observed at higher values of α (see Figure 6b, case 4) is due to the vitrification of the resin. The effects of this vitrification are even more evident in Figure 4, where the function $F_2(\alpha)$ shows a sudden drop at a certain value of α. As the cure progresses

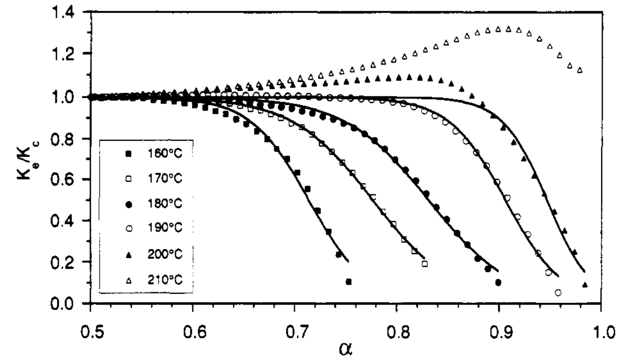

Figure 7. "Diffusion factor" obtained by dividing experimental values for $d\alpha/dt$ by values predicted according to chemical kinetic model. Symbols correspond to experimental points, lines to regression fit obtained with eq 15.

and the resin cross-links, the glass transition temperature T_g of the system rises. When it approaches the curing temperature, the resin passes from a rubbery to a glassy state, the mobility of the reacting groups is hindered, and the reaction is controlled by diffusion rather than by chemical factors. Various workers have attempted mathematical treatments of this phenomenon.[29-35] A typical approach[31] is to express T_g in terms of α using Di Benedetto's equation and then to express the diffusion-controlled rate constant in terms of $T-T_g$ by a Williams-Landel-Ferry type equation. Thus the overall relationship is rather complex. Chern and Poehlein have recently proposed a somewhat simpler semiempirical relationship based on free volume considerations.[30] When the degree of cure reaches a certain critical value α_c, diffusion control takes over and the diffusion-controlled rate constant K_d is given by

$$K_d = K_c \exp[-C(\alpha - \alpha_c)] \qquad (13)$$

where K_c is the rate constant for non-diffusion-controlled (chemical) kinetics and C is a constant. This equation corresponds to a rather abrupt onset of diffusion control at $\alpha = \alpha_c$. In reality, the onset is somewhat more gradual and there is a region where both chemical and diffusion control are significant. According to Rabinowitch,[36] the overall effective rate constant K_e can be expressed in terms of K_d and K_c as follows:

$$\frac{1}{K_e} = \frac{1}{K_d} + \frac{1}{K_c} \qquad (14)$$

Combining eqs 13 and 14, we can define a "diffusion factor" $f(\alpha)$ as follows:

$$f(\alpha) = \frac{K_e}{K_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \qquad (15)$$

The effective reaction rate is equal to the chemical reaction rate multiplied by this factor, which follows an S-shaped curve. For values of α significantly lower than α_c, $f(\alpha)$ is approximately equal to 1 and diffusion control is negligible. When α approaches α_c, $f(\alpha)$ begins to decrease, reaching 0.5 when $\alpha = \alpha_c$. Beyond this point it continues to decrease, eventually approaching zero, so that the reaction becomes very slow and effectively stops. In this work, data for $f(\alpha)$ were obtained by dividing the experimental values of $d\alpha/dt$ by those predicted on the basis of the chemical kinetic model. Figure 7 shows the results for one experiment at each temperature. The dropoff in rate due to the onset of diffusion control is obvious. An interesting phenomenon is observed at higher temperatures. At 200 °C, when α is greater than 0.6 the reaction rate increases slightly (by about 10%) above that predicted by the model, before it drops off because of diffusion control. At 210 °C, a similar effect is observed but it is much more pronounced. This is believed to be due to another reaction, not included in the model, which becomes important only at higher temperatures. The same phenomenon has been reported by Mijovic et al.[15] for an MY 720/HT 976 mixture cured at 210 °C. On the basis of FT-IR results, Morgan et al.[10] have suggested that at temperatures greater than 200 °C two hydroxyl groups combine with loss of water to form an ether group, and this could explain the results. Values of C and α_c in eq 15 were determined by applying nonlinear regression to the data for K_e/K_c for temperatures between 160 and 200 °C. Except for the slight deviation at 200 °C just mentioned, very good agreement was obtained, as shown in Figure 7.

Figure 8 shows the results for one experiment at each temperature when the experimental values of $d\alpha/dt$ are compared to those calculated by the model (case 4), with the diffusion factor included. Except for the deviations previously mentioned, the agreement is excellent. The average constants obtained from the analysis are summarized in Table III, together with the standard deviations. The corresponding Arrhenius plots of ln K versus $1/T$ are shown in Figure 9. Individual data points for the three experiments at each temperature are shown in order to give an indication of the scatter. Good linear correlations are observed, which lead to the parameters given in Table IV. The activation energies for the X-catalyzed and hydroxyl-catalyzed epoxide–amine reactions are 61.4 and 72.5 kJ/mol, respectively, while that for the etherification reaction is significantly higher at 101.4 kJ/mol. These values are very similar to those obtained by Chiao.[21] The variation of the quantities α_c and C with temperature is shown in Figure 10. For α_c, the relationship can be considered linear within experimental error, and regression gives the following equation (squared correlation coefficient 0.987):

$$\alpha_c = 0.005376T - 0.1350 \qquad (16)$$

where T is expressed in degrees Celsius. Thus the diffusion factor defined in eq 15 is also a function of temperature. For the coefficient C, there is considerably more scatter, and no discernible trend with temperature is observed. The average value for the experiments from 160 to 190 °C is 30.1 (standard deviation 5.1). The values for 200 °C were not used in the averaging because of the slight deviation observed at this temperature, attributed to the hydroxyl–hydroxyl condensation reaction.

Summary of the Model and General Discussion. It has been shown that an excellent fit to the experimental DSC data for the curing of Narmco 5208 in the temperature range 160–200 °C is obtained by using a model based on the following assumptions: (i) a reaction between primary amine and epoxide groups (PA–E) that produces secondary amine and hydroxyl groups and that is catalyzed both by groups initially present in the resin (rate constant K_1) and by the hydroxyl groups formed in the reaction (rate constant K_2); (ii) a similar reaction between secondary amine and epoxide groups (SA–E), whose rate constant is one-half of that for the previous reaction; (iii) a reaction between epoxide and hydroxyl groups that is catalyzed by the tertiary amine groups formed in the SA–E reaction (rate constant K_3); (iv) a diffusion control correction factor for which a semiempirical equation is given and which becomes important when the degree of conversion approaches a certain critical value α_c, which is dependent on the temperature.

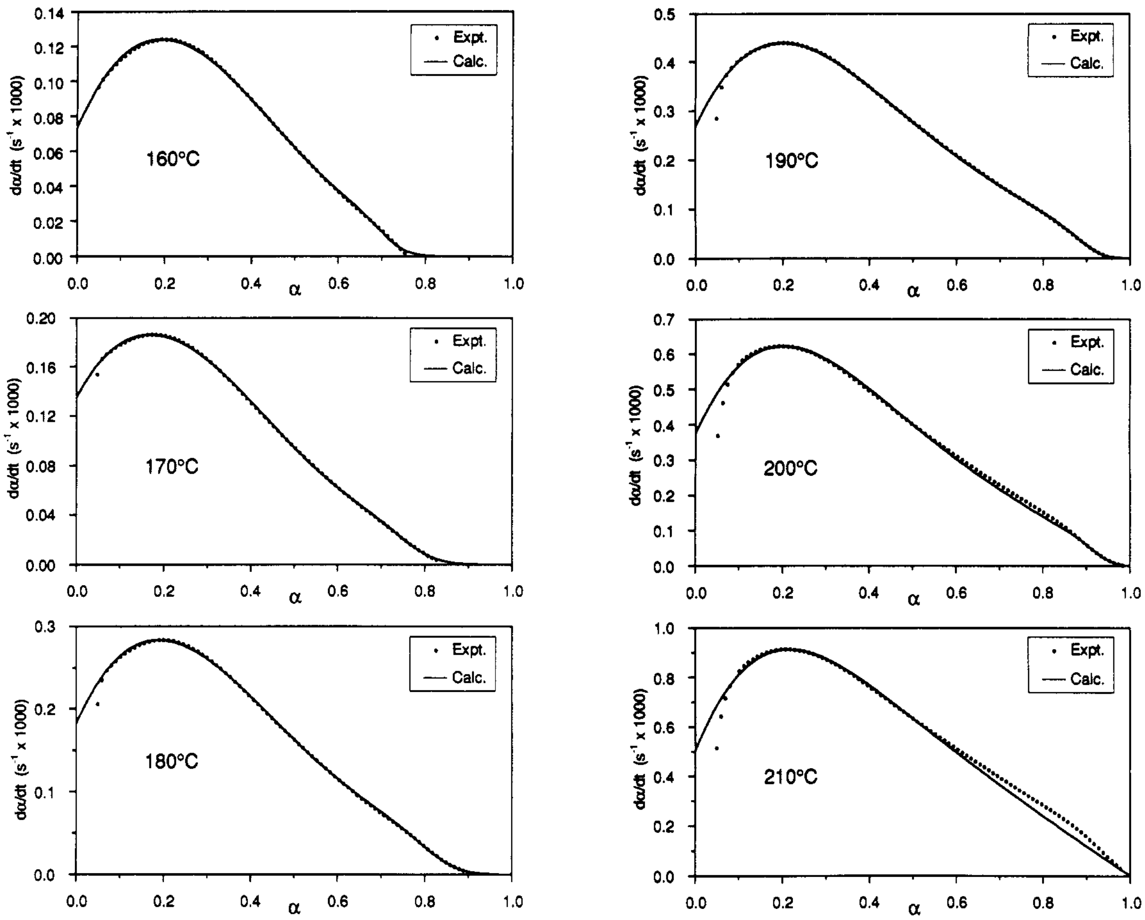

Figure 8. Comparison of experimental values of $d\alpha/dt$ with curves calculated according to the proposed model, including diffusion control, for six temperatures.

Table III
Average Constants (with Standard Deviations in Parentheses) for the Proposed Model[a]

temp, °C	K_1, $s^{-1} \times 1000$	K_2, $s^{-1} \times 1000$	K_3, $s^{-1} \times 1000$	α_c	C
160	0.134 (0.011)	1.232 (0.057)	0.062 (0.008)	0.725 (0.012)	34.7 (7.2)
170	0.238 (0.014)	1.682 (0.056)	0.112 (0.007)	0.779 (0.002)	26.7 (1.2)
180	0.321 (0.026)	2.750 (0.053)	0.218 (0.023)	0.827 (0.005)	27.0 (2.0)
190	0.474 (0.025)	4.199 (0.235)	0.444 (0.070)	0.898 (0.016)	31.9 (4.3)
200	0.602 (0.026)	6.288 (0.231)	0.637 (0.061)	0.934 (0.020)	40.6 (9.0)
210	0.836 (0.004)	9.503 (0.037)	1.130 (0.038)		

[a] Values in parentheses correspond to standard deviations based on three determinations.

The progress of the polymerization is described in terms of two parameters, α and β. The first (α) is the overall degree of conversion as expressed in terms of the fraction of epoxide groups reacted. The second (β) is the fraction of amine N-H bonds that have reacted. These two quantities are closely interrelated and their evolution with time is given by the following equations:

$$d\beta/dt = [(K_1 + BK_2\beta)(1 - \beta)](1 - \alpha)f(\alpha,T) \quad (17)$$

$$d\alpha/dt = [B(K_1 + BK_2\beta)(1 - \beta) + K_3\beta^3](1 - \alpha)f(\alpha,T) \quad (18)$$

where the diffusion control factor $f(\alpha,T)$ is given by

$$f(\alpha,T) = [1 + \exp(30.1\alpha + 4.06 - 0.1617T)]^{-1} \quad (19)$$

with T expressed in degrees Celsius. Equations 17 and 18 correspond to case 4 of the general model ($m = n = 1$) with $Y = Z = 0$. Equation 19 is obtained by combining eqs 15 and 16. If the reaction is carried out at constant temperature, the relationship between α and β is described by eq 11. The quantity B is the ratio of amine N-H bonds to epoxide rings, and for a typical lot of Narmco 5208 it is equal to 0.60. Also, the initial degree of conversion α_0 in Narmco 5208 is not zero because of resin advancement during the manufacturing process (B-staging) and possibly during subsequent handling. Typical values for a newly received batch are $\alpha_0 = 0.038$ and $\beta_0 \approx \alpha_0/B = 0.063$. Accurate values may be determined for a given batch by physicochemical analysis.

The three rate constants obey the well-known Arrhenius relationship $K_i = A_i \exp(-E_{ai}/RT)$ and may be calculated from the parameters given in Table IV.

The amount of heat produced by 1 g of Narmco 5208 resin on going from $\alpha = 0$ to $\alpha = 1$ is 645 J. This is based on the true resin weight, exclusive of volatile components (solvent and moisture).

Some discussion is in order concerning the assumptions of the model. Assumption ii referred to above implies that the secondary amine groups show the same reactivity with respect to epoxide as the primary amine groups. This important question has been extensively studied, and the results have been summarized by various authors.[4,26,37] While many of the experimental values that have been reported for this ratio are close to 0.5, others are significantly lower, especially in the case of aromatic amines. However, as was recently pointed out by Charlesworth,[38] much of the earlier data were obtained by using dilute

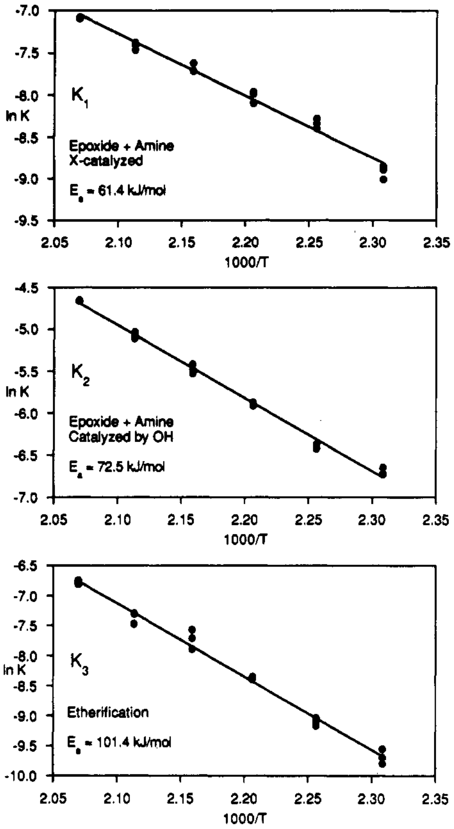

Figure 9. Arrhenius plots for the rate constants determined from the analysis.

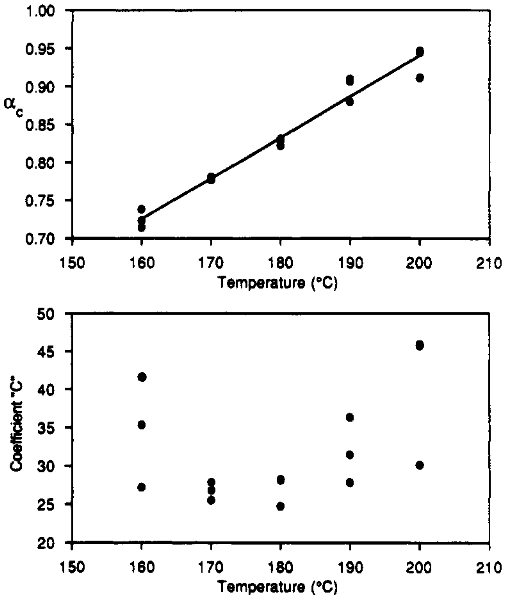

Figure 10. Dependence of α_c and the coefficient C (eq 15) on temperature, T.

Table IV
Arrhenius Parameters for the Proposed Model

rate const, s^{-1}	ln A	E_a/R, K	E_a, kJ/mol
K_1	8.243	7389	61.4
K_2	13.36	8719	72.5
K_3	18.53	12221	101.4

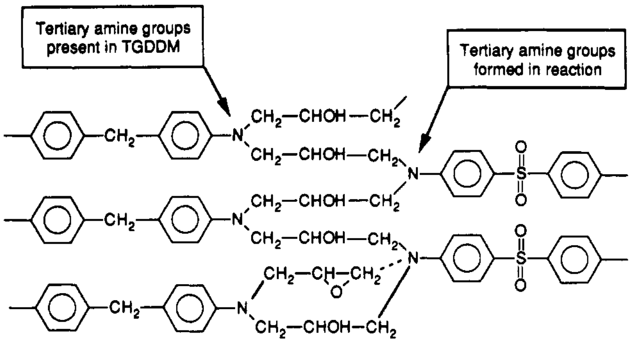

Figure 11. Structure of the cross-linked polymer formed by reaction between TGDDM and DDS.

solutions in alcohol, and it is known that alcohols have a strong catalytic effect on epoxide ring opening reactions. Hence the situation in alcohol solution may be quite different from that in bulk mixtures involving no solvent. In fact, data obtained by Charlesworth[37,38] and by other workers[39,40] on bulk mixtures of epoxy resin and aromatic amines suggest that the assumption of equal reactivity can be quite valid in such cases. In the specific case of TGDDM and DDS, as mentioned in the Introduction, there are conflicting results in the literature and the question will only be resolved through further work.

Assumption iii implies that the etherification reaction proceeds through a ternary complex involving epoxide, hydroxyl, and tertiary amine groups. This is not unreasonable, since both hydroxyl and tertiary amine groups are known to accelerate the etherification reaction.[41-44] In fact it is the same type of complex proposed for the hydroxyl-catalyzed epoxide–amine reaction, except that when the amine group bears a hydrogen atom the reaction follows a different path. It is interesting, however, that the best fit to the experimental data is obtained if it is assumed that the tertiary amine groups produced in the reaction are more effective in catalyzing the etherification than are those initially present in the TGDDM. Figure 11 shows the structure of the polymer formed by the TGDDM–DDS reaction. The tertiary amine groups formed in the reaction originate from the DDS and are attached to a phenyl ring with an SO_2 group in the para position. The groups initially present, however, are in the TGDDM and are attached to a phenyl ring with a CH_2 group in the para position. The strong effect of such groups on kinetics, even though they may be far from the reactive site, is well-known. For example, Tanaka et al.[42] found that the rate of reaction of the epoxy compound phenyl glycidyl ether with different substituents in the para position varied by a factor of 4. Thus it is not unreasonable to postulate that the two types of tertiary amine groups shown in Figure 11 might have widely different reactivities, given the different electronic nature of the SO_2 and CH_2 groups. If this is the case, though, it is difficult to argue that the tertiary amine groups from the DDS should be more active, because the electron-withdrawing nature of the SO_2 groups would be expected to make them less nucleophilic. A more plausible explanation may exist based on steric arguments. The newly formed tertiary amine groups are located in a position where they can bring about intramolecular catalysis of reactions of the remaining epoxide ring, as shown at the bottom of Figure 11. Dušek and Matějka have used this argument to explain the apparent enhanced reactivity of the second epoxide ring in N,N'-diglycidyl amines.[45,46] Their detailed study of N,N'-diglycidylaniline showed that intramolecular etherification is significant and occurs faster than the intermolecular reaction. Similar results have been obtained by others[47] and it has been suggested that intramolecular reaction and ring formation are quite important in the TGDDM-DDS system.[11] These arguments provide some support for assumption iii of our model.

Although vitrification was found to have a profound effect on the kinetics, no effects were observed that might

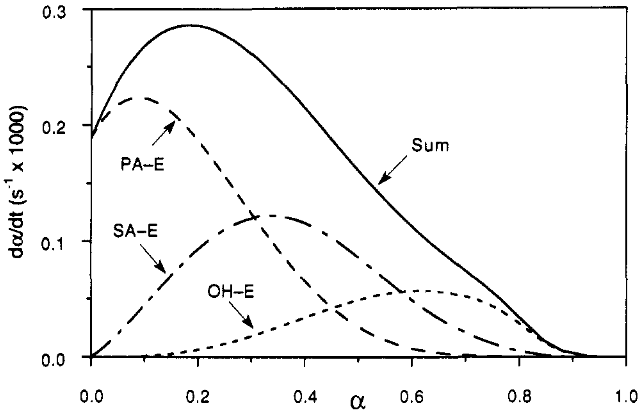

Figure 12. Calculated curves for $d\alpha/dt$ as a function of α at 180 °C, showing the separate contributions from the PA–E, SA–E, and OH–E reactions.

be due to gelation, which occurs at lower values of α. It may be that because the epoxide–amine reaction is predominant before gelation and etherification afterward, the corresponding rate constants reflect the state of the resin at each stage. However, it is more likely that, as has been suggested by others, diffusion control becomes important only on vitrification and not on gelation.[48,49]

It is interesting to compare our results with those of Chiao.[21] In both cases, a good fit was obtained by varying three rate constants, one of which corresponds to the etherification reaction. However, the assumptions made are different. In our case, we assume equal reactivity of primary and secondary amine groups; this makes it possible to partly solve the kinetic equations and develop certain analytical expressions to model the cure. In Chiao's case, he assumes a fixed value for the ratio of the rate constants for hydroxyl-catalyzed and noncatalyzed amine addition, on the basis of results obtained on a different epoxy amine system. This is questionable because the "noncatalyzed" reaction, at least in the case of commercial materials, is generally acknowledged to involve catalysis by impurities present in the resin, and their type and concentration may vary substantially from one system to another. Thus both treatments are subject to some question, and the fact that a good fit is obtained in both cases suggests that the DSC data are not greatly sensitive to either. Only further work will determine which approach is more valid for the TGDDM-DDS system.

Two factors have been neglected in our treatment, which may have some influence on the results. The first is the presence of the minor epoxy resin in Narmco 5208; it is known to be somewhat more reactive than the major resin.[3] The second is the presence in the kinetics equations of the coefficient Y, which is related to the concentration of hydroxyl groups initially present in the resin. In this work it was assumed to be negligible, as no experimental value was available. It would be interesting to further refine the model by doing a study of the binary TGDDM-DDS system in which the initial concentration of hydroxyl groups is determined and included in the model.

Calculated Results. With the proposed model, it is possible to perform calculations in order to better understand how the system behaves in different circumstances. For example, Figure 12 shows the predicted curve for $d\alpha/dt$ as a function of α for isothermal curing at 180 °C, including the effects of vitrification, which occurs around $\alpha_c = 0.83$. The curve is decomposed to show the contributions from the three different reactions involved, namely, PA–E, SA–E, and OH–E. The figure clearly shows why the approximation mentioned earlier, in which the reaction is separated into two distinct stages, is not really applicable. The general behavior is the same regardless of the temperature. For α = 0–0.2 the OH–E contribution is negligible and the approximation is valid. Between 0.2 and 0.8, however, all three reactions are significant. From 0.2 to 0.6, the epoxide–amine reactions are more important than the OH–E reaction. At α = 0.6 the PA–E reaction becomes negligible and the OH–E reaction becomes the most important. Finally, at α around 0.8, the SA–E reaction becomes negligible. Only then could eq 6 serve as a good approximation, but it cannot be used because in the real system vitrification occurs near this point and the reaction becomes diffusion-controlled. Thus, in spite of the significant difference in activation energy for the amine and etherification reactions, the two cannot be clearly separated in time. This description of the curing process is in general agreement with the findings of Morgan and Mones for TGDDM-DDS, as illustrated in Figure 10 of ref 11.

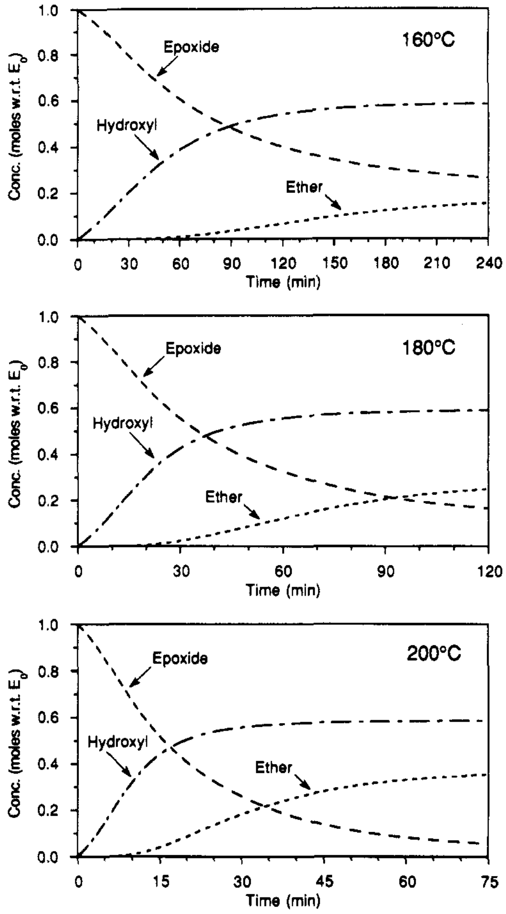

Figure 13. Calculated concentrations of epoxide, hydroxyl, and ether groups as a function of time for isothermal curing at 160, 180, and 200 °C.

It is also possible to predict the evolution of the cure with time, by applying eqs 17 and 18 on an incremental basis. The concentrations of the different species can be calculated from α and β by means of the equations given in the preceding paper.[2] Figures 13 and 14 show the predicted concentrations of the different species as a function of time for isothermal curing at 160, 180, and 200 °C. In all three cases, there is a "turning point" around α = 0.45. This occurs after 71 min at 160 °C, 30 min at 180 °C, or 14 min at 200 °C. At this point, over 90% of the primary amine groups have disappeared but ether formation is just starting to become important. However, the SA–E reaction, which produces tertiary amine groups, is significant both before and after this point. The main

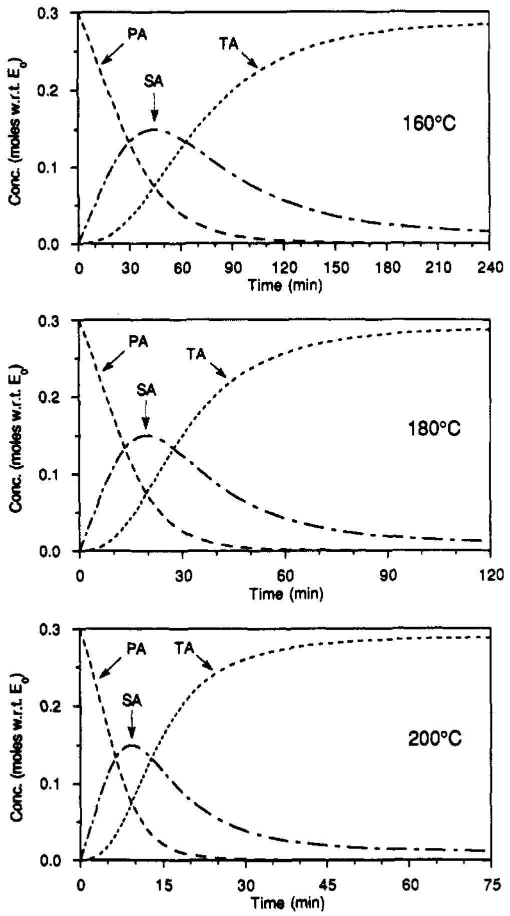

Figure 14. Calculated concentrations of primary amine (PA), secondary amine (SA), and tertiary amine (TA) groups as a function of time for isothermal curing at 160, 180, and 200 °C.

effect of temperature is that, beyond the turning point, at higher temperatures the conversion of epoxide to ether proceeds faster and to a greater extent. At 160 °C, the critical value for diffusion control ($\alpha_c = 0.72$) is reached after 218 min. At this point, 58% of the epoxide groups have reacted with amine, 14% have reacted with hydroxyl, and 28% remain unreacted. At 180 °C, α_c (=0.83) is reached after 117 min, at which point 59% of epoxide groups have reacted with amine, 24% have reacted with hydroxyl, and 17% are unreacted. Finally, at 200 °C, α_c (=0.94) is reached after 73 min, where 59% of epoxide groups have reacted with amine, 35% have reacted with hydroxyl, and 6% are unreacted. Thus at the point where vitrification slows down the reaction significantly, the epoxide–amine reaction is virtually complete, regardless of temperature, but the epoxide–hydroxyl reaction is only partially complete. At higher temperatures, more ether linkages are formed, as expected. After vitrification, the cure proceeds at an ever-decreasing rate, so that complete cure may not be achieved. After twice the time required to reach α_c, the degree of cure is calculated to be 78% at 160 °C, 89% at 180 °C, and 98% at 200 °C.

Finally, to illustrate the overall accuracy of the model, Figure 15 shows the evolution of α with time at three different temperatures, comparing the behavior predicted by the *general* model with the results for the three individual DSC experiments.

Conclusion

A mechanistic model has been proposed for the kinetics of polymerization of Narmco 5208, which consists mainly of the epoxy resin bis[4-(diglycidylamino)phenyl]methane

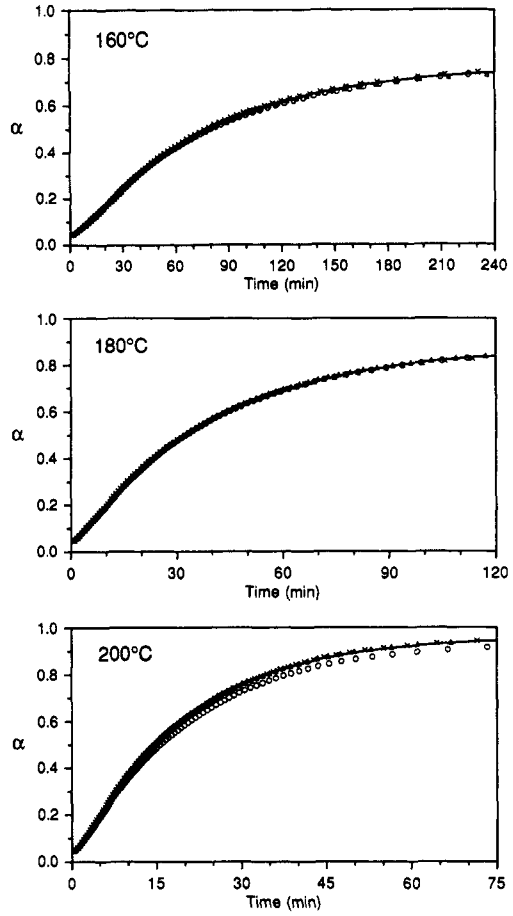

Figure 15. Evolution of α with time at three different temperatures, as predicted by the general model (line) and as measured in three separate DSC experiments (○, ×, △).

(TGDDM) and the amine hardener bis(4-aminophenyl) sulfone (DDS). This model represents a significant improvement over much of the previously published work in that it explicitly takes into account both the epoxide–amine reactions and the subsequent etherification reaction. The kinetics are completely described in terms of three rate constants, which were determined to fit the data. The best fit was obtained on the assumption that the etherification reaction is catalyzed by the tertiary amine groups formed in the epoxide–amine reaction; further experimental work is required to confirm this. The rate constants obey the Arrhenius relationship and values of the preexponential factor A and the activation energy E_a have been determined. These are specific to the Narmco 5208 system, but the general approach could be applied to any amine-cured system.

Apart from the three rate constants, no other parameters were varied to fit the data. The amine-to-epoxide ratio B was assigned a value determined by independent means (liquid chromatography) and was not varied as in some previous work.[5] Furthermore, the kinetics were assumed to be first order with respect to all participating species, and it was not necessary to introduce noninteger exponents as in the widely used eq 7. Although the model is thus less empirical than previous ones, it gives an excellent fit to the experimental data for all values of the degree of conversion α up to the critical point where the resin vitrifies and the reaction becomes diffusion-controlled. To describe the cure in this region, a diffusion factor has been introduced on the basis of a combination of two equations proposed by other workers.[30,36] With the inclusion of this factor, it is possible to calculate with excellent precision the degree of conversion over the whole range of cure and over the temperature range 160–200 °C, which covers the usual curing conditions.

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References and Notes

(1) Roberts, R. W. *SAMPE J.* **1987**, *23* (5) (Sept./Oct.), 28.

(2) Cole, K. C. *Macromolecules*, preceding paper in this issue.

(3) Chu, H. S.; Seferis, J. C. *Polym. Compos.* **1984**, *5*, 124.

(4) Barton, J. M. *Adv. Polym. Sci.* **1985**, *72*, 111.

(5) Lee, W. I.; Loos, A. C.; Springer, G. S. *J. Compos. Mater.* **1982**, *16*, 510.

(6) Cizmecioglu, M.; Gupta, A. *SAMPE Q.* **1982**, *13* (2) (April), 16.

(7) Moacanin, J.; Cizmecioglu, M.; Tsay, F.; Gupta, A. *Org. Coat. Appl. Polym. Sci. Proc.* **1982**, *47*, 587.

(8) Gupta, A.; Cizmecioglu, M.; Coulter, D.; Liang, R. H.; Yavrouian, A.; Tsay, F. D.; Moacanin, J. *J. Appl. Polym. Sci.* **1983**, *28*, 1011.

(9) Mones, E. T.; Walkup, C. M.; Happe, J. A.; Morgan, R. J. *Proc. Natl. SAMPE Techn. Conf.* **1982**, *14*, 89.

(10) Morgan, R. J.; Happe, J. A.; Mones, E. T. *Proc. Natl. SAMPE Symp./Exhib.* **1983**, *28*, 596.

(11) Morgan, R. J.; Mones, E. T. *J. Appl. Polym. Sci.* **1987**, *33*, 999.

(12) Zukas, W. X.; Schneider, N. S.; MacKnight, W. J. *Polym. Mat. Sci. Eng.* **1983**, *49*, 588.

(13) Apicella, A.; Nicolais, L.; Iannone, M.; Passerini, P. *J. Appl. Polym. Sci.* **1984**, *29*, 2083.

(14) Stark, E. B.; Seferis, J. C.; Apicella, A.; Nicolais, L. *Thermochim. Acta* **1984**, *77*, 19.

(15) Mijovic, J.; Kim, J.; Slaby, J. *J. Appl. Polym. Sci.* **1984**, *29*, 1449.

(16) Mijovic, J. *J. Appl. Polym. Sci.* **1986**, *31*, 1177.

(17) Barton, J. M. *Br. Polym. J.* **1986**, *18*, 37.

(18) Barton, J. M. *Br. Polym. J.* **1986**, *18*, 44.

(19) Grenier-Loustalot, M.-F.; Mouline, G.; Grenier, P. *Polymer* **1987**, *28*, 2275.

(20) Dusi, M. R.; Lee, W. I.; Ciriscioli, P. R.; Springer, G. S. *J. Compos. Mater.* **1987**, *21*, 243.

(21) Chiao, L. *Macromolecules* **1990**, *23*, 1286.

(22) Bell, J. P. *J. Polym. Sci., Part A-2* **1970**, *6*, 417.

(23) Shechter, L.; Wynstra, J.; Kurkjy, R. P. *Ind. Eng. Chem.* **1956**, *48*, 94.

(24) Cole, K. C.; Noël, D. National Research Council Canada Publication No. 29449, IGM88RT-101-772-G, Sept 1988.

(25) Noël, D.; Hechler, J.-J.; Cole, K. C.; Chouliotis, A.; Overbury, K. C. *Thermochim. Acta* **1988**, *125*, 191.

(26) Rozenberg, B. A. *Adv. Polym. Sci.* **1986**, *75*, 113.

(27) Horie, K.; Hiura, H.; Sawada, M.; Mita, I.; Kambe, H. *J. Polym. Sci., Part A-1* **1970**, *8*, 1357.

(28) Kamal, M. R. *Polym. Eng. Sci.* **1974**, *14*, 231.

(29) Havliček, I.; Dušek, K. Crosslinked Epoxies *Proc. Discuss. Conf., 9th* **1986**, 417.

(30) Chern, C.-S.; Poehlein, G. W. *Polym. Eng. Sci.* **1987**, *27*, 788.

(31) Kim, D. H.; Kim, S. C. *Polym. Bull.* **1987**, *18*, 533.

(32) Rohr, D. F.; Klein, M. T. *Ind. Eng. Chem. Res.* **1988**, *27*, 1361.

(33) Matsuoka, S.; Quan, X.; Bair, H. E.; Boyle, D. J. *Macromolecules* **1989**, *22*, 4093.

(34) Pascault, J. P.; Williams, R. J. J. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 85.

(35) Pang, K. P.; Gillham, J. K. *J. Appl. Polym. Sci.* **1990**, *39*, 909.

(36) Rabinowitch, E. *Trans. Faraday Soc.* **1937**, *33*, 1225.

(37) Charlesworth, J. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 621.

(38) Charlesworth, J. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 731.

(39) Grenier-Loustalot, M.-F.; Grenier, P. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 4011.

(40) Sung, C. S. P.; Pyun, E.; Sun, H.-L. *Macromolecules* **1986**, *19*, 2922.

(41) Tanaka, Y.; Bauer, R. S. In *Epoxy Resins: Chemistry and Technology*, 2nd ed.; May, C. A., ed.; Marcel Dekker: New York, 1988; Chapter 3.

(42) Tanaka, Y.; Tomio, M.; Kakiuchi, H. *J. Macromol. Sci. (Chem.)* **1967**, *A1*, 471.

(43) Smith, I. T. *Polymer* **1961**, *2*, 95.

(44) Gross, A.; Kollek, H.; Brockmann, H. *Int. J. Adhes. Adhes.* **1988**, *8*, 225.

(45) Dušek, K.; Matějka, L. *Polym. Mater. Sci. Eng.* **1987**, *56*, 356.

(46) Matějka, L.; Dušek, K. *Macromolecules* **1989**, *22*, 2902, and 2911.

(47) Ancelle, J.; Attias, A. J.; Bloch, B.; Lauprêtre, F.; Monnerie, L. *Makromol. Chem., Macromol. Symp.* **1987**, *9*, 123.

(48) Prime, R. B. In *Thermal Characterization of Polymeric Materials*, Turi, E. A. Ed.; Academic Press: New York, 1981; Chapter 5.

(49) Riccardi, C. C.; Williams, R. J. J. Crosslinked Epoxies. *Proc. Discuss. Conf., 9th* **1986**, 291.